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FRACTAL-LIKE BUT NON-FRACTAL BEHAVIOR OF ONE STEP
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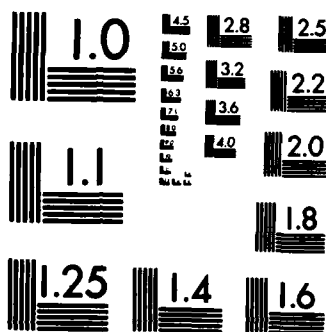
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TECHNICAL REPORT NO. 45

"Fractal-like", but Non-fractal, Behavior of One Step Dipolar Energy
Transfer on Regular Lattices with Excluded Volume"

by

C. L. Yang, P. Evesque and M. A. El-Sayed

The Journal of Physical Chemistry, in press

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"FRACTAL-LIKE", BUT NON-FRACTAL, BEHAVIOR OF ONE STEP DIPOLAR ENERGY
TRANSFER ON REGULAR LATTICES WITH EXCLUDED VOLUME

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ABSTRACT:

simulation calculation is carried out for the time dependence of the donor intensity as one-step acceptor trapping process on a simple cubic lattice of interconnected rods of dimensions comparable to those found for the pores of Vycor (Corning glass 7930). The donor and acceptor are allowed to occupy random sites on the surface of the pore. The results are fitted using the equations of Blumen and Klafter¹ for energy transfer on a fractal structure. An "apparent fractal" dimension, $\langle d' \rangle$, is determined which is shown to result from an excluded volume effect and is not due to a real fractal structure. $\langle d' \rangle$ is found to depend slightly on time, the acceptor concentration, and the length:width ratio of the pores.

⁺⁺ In partial fulfillment of the Ph. D. degree

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INTRODUCTION

Fractals², structures with a dilation symmetry, have attracted a great deal of attention recently. This is due to their utility for describing disordered systems. They have been used to describe systems in polymer^{3,4}, protein^{4,5} and surfaces science⁶, and processes such as crystal growth⁷, dielectric breakdown⁸, turbulence and chaos⁹. Fractals also have been used to describe the diffusion of liquids into porous media¹⁰.

At least three different dimensions are required to define a fractal^{11,12}. The first is the Euclidean dimension, d , in which the structure is embedded. The second is called the fractal dimension², D . This describes the dependence of the number of sites $N(R)$ on the distance R , through the relation ($N(R) = R^D$). The third dimension is the spectral or fracton dimension^{11,12}, d , which governs the random walk and relaxation processes and determines the density of states of the structure. The spectral dimension has been previously discussed in electron-spin relaxation studies in proteins^{4,5} and triplet-triplet annihilation studies in mixed molecular crystals^{13,14}. More recently, studies of one step electronic energy transfer have been discussed, both theoretically¹ and experimentally¹⁵, in terms of the fractal dimension D .

Energy transfer between Rhodamine B and Malchite green doped into Corning Vycor glass (7930) has been experimentally¹⁵ analyzed in terms of the Klafter and Blumen¹ equation relating the fractal dimension to the temporal behavior of the donor intensity. A fractal dimension of 1.74 ± 0.12 has been determined. Electron microscopic studies¹⁶ of the Corning 7930 Vycor glass showed that Vycor glass is a rather compact packing of spheres whose diameters are narrowly distributed around 200 Å. This packing is consistent with other results such as

the pore size distribution, which is found to be sharp (with a diameter of $40 \pm 3 \text{ \AA}$)¹⁵, and the volume fraction of pores, which constitutes only 25-to-30 % of the total volume¹⁵.

The above observations together with the fact that donor and acceptor molecules have finite thicknesses ($\sim 5 \text{ \AA}$) justify representing the structure of the pores in Vycor by a three dimensional simple cubic lattice of interconnected rods, each having a diameter of 40 \AA (the pore diameter) and a length of 200 \AA (the diameter of the spheres). With this structure, we carried out simulation calculations of the decay of the donor intensity resulting from a one step dipole-dipole energy transfer to acceptors. The results were then fitted to the Blumen-Klafter equation¹ and an "apparent fractal" dimension was determined. The latter, as expected for a non-fractal structure, is found to depend on time, the acceptor concentration, and the length:width ratio. However, within the range of times and concentrations normally available to experimentalist, an "apparent constant fractal" dimension can be inferred. At very long times and/or at very low acceptor concentrations (conditions that cannot be reached experimentally due to the limitations imposed by the value of the radiative lifetime of the donor), a dimensionality of 3.0 is observed. These findings are the result of the excluded volume (of the spheres) and the excluded surface (due to surface of contact between spheres) and are not due to the fractal structure.

The Model

We consider only the one step dipole-dipole donor-to-acceptor transfer. Donor-donor energy transfer is excluded. Furthermore, the energy levels of the donor and acceptor and the temperature are such that no acceptor to donor back

transfer is allowed.

Consider the case of one excited donor located at a position \vec{R}_D which is surrounded by a statistical distribution $P_A(\vec{R}_D, \vec{R}_A)$ of acceptors at position \vec{R}_A . These acceptors can trap the donor excitation in a trapping time $\tau_t(\vec{R}_A - \vec{R}_D)$ which depends on the relative distance $\vec{R}_A - \vec{R}_D$ between the acceptors and the donors. It can be shown that the decay curve of the donor excitation follows the equation^{17,18}:

$$I_{\vec{R}_D}^*(t) = \exp\left(-\frac{t}{\tau_0}\right) + \int d\vec{R}_A P_A(\vec{R}_D, \vec{R}_A) \left[1 - \exp\left(-\frac{t}{\tau_t(\vec{R}_A - \vec{R}_D)}\right)\right] \quad (1)$$

where τ_0 is the donor lifetime in the absence of acceptor and $d\vec{R}_A$ is the volume element over which the integration is performed. Equation (1) has been used previously assuming all donor positions are equivalent. In our structure, this is not true since short time coupling to acceptor distribution is different for donors positioned at rod intersections from those situated in the middle of the rods. For this reason, averaging over the donor position seems necessary. The averaging of equation (1) over the positions of the donors with distribution $P_D(\vec{R}_D)$ leads to the result:

$$I_D(t) = \int d\vec{R}_D P_D(\vec{R}_D) \exp\left(-\frac{t}{\tau_0}\right) + \int d\vec{R}_A P_A(\vec{R}_D, \vec{R}_A) \left[1 - \exp\left(-\frac{t}{\tau_t(\vec{R}_A - \vec{R}_D)}\right)\right] \quad (2)$$

with $\tau_t(\vec{R}_A - \vec{R}_D) = \tau_1 \left(\frac{|\vec{R}_A - \vec{R}_D|}{R_0}\right)^\epsilon$. In order to simplify the integration, we have represented the narrow distribution of the radii of the spheres, by a regular distribution of the centers of the spheres on a simple cubic lattice, whose spacing is equal to twice the radius of a sphere, R_0 . Electronic energy transfer from donors to acceptors lying either on the same sphere or on two different spheres are allowed. As no molecule can occupy sites on surface of a contact between any two spheres due to the thickness of a molecule ($\sim 5 \text{ \AA}$), an

excluded surface effect is expected. We took this into account by transforming the lattice of spheres into a lattice of rods, interconnected and directed along the three axis of the cubic lattice. The lengths of the rods are equal to the diameter of the sphere and their diameters are equal to the pore diameters. Donors and acceptors are allowed to occupy random sites on the surface of these rods.

RESULTS AND DISCUSSION

The simulation consists of calculating $I_D(t) e^{(t/\tau_c)}$ using Eq.(2) at different times t ; for different acceptor concentrations, p_A ; and for different rod length:width ratio (L/W). The numerical integration was carried out on the surface where the donors and acceptors are randomly distributed. This represents the time dependence of the donor intensity resulting only from energy transfer processes (and not from first-order decay).

In order to fit our simulation, we have used the equation previously derived¹:

$$I_D(t) = \exp \left\{ -\left[\frac{t}{\tau_c} + p_A A \left(\frac{t}{\tau_c} \right)^d \right] \right\} \quad (3)$$

For dipole-dipole transfer, $s = 6$; A is a time independent¹ function; and d is the Euclidean or fractal (D) dimensionality depending on the structure of the system studied. This equation has been used by Even et al¹⁵ to fit experimental data for energy transfer between Rhodamine B and Malchite green on Vycor and gave $D = 1.74 \pm 0.12$.

It is obvious that the simulation of the temporal behavior of the donor intensity in our model should not, and indeed does not, follow a simple decay

law of the form of Eq. (3) in a strict sense. Thus, the exponent of the time in Eq. (3) cannot be D , since we selected a cubic and not a fractal lattice. As will be shown below, this exponent does not have to be integer at all times or acceptor concentrations; thus, it cannot be d . Let us call it d' . It is found, as expected, that d' depends on the time and on the acceptor concentration. In order to determine the time and concentration dependences of this exponent, the negative logarithm of the calculated intensity has been plotted versus time on a \ln - \ln plot for different acceptor concentrations (see fig. 1). In such plots, the slopes of the curves are equal to $d'/6$. Although Fig. 1 shows that $d'/6$ depends on the time, it also shows that it is approximately constant for a given range of time, concentration, and $L:W$. This allows us to use Eq. (3) to determine an average value of d' , $\langle d' \rangle$, for structures such as the one we are presently using.

It is then possible that, on Vycor-like structures, the decay can be described with a pseudo-constant exponent. For instance, most experimental results are obtained during the time required for the initial intensity to decrease by at most a factor of 100. During this time range, the value $\langle d' \rangle$ is apparently constant.

From Fig. (1), the best value of $\langle d' \rangle$ is determined for the different time and concentration range of interest. With these values, equation (3) is then tested; and the results are shown in Fig. (2) which gives a straight line for $\ln I$ vs. $t^{\langle d' \rangle/6}$.

Table 1 gives the values of $\langle d' \rangle$ for the different concentrations and $L:W$ for the time range required for the donor intensity to decay to 1/100 of its initial value. In this table, the transfer decay times (τ_e) in units of a critical transfer time (τ_1), the time of transfer at a donor-acceptor distance

of the sphere radius, R_0 , are also given for different concentrations and L:W values. As expected, as the L:W ratio increases, $\langle d^1 \rangle$ decreases, and, eventually, one-dimensional behavior is observed. Also, as the concentration decreases (or the time increases), the effects of the excluded volume and surface disappears; and three-dimensional behavior is recovered.

The approximate simulation above shows that $\langle d^1 \rangle = 1.7$ (the value determined experimentally)¹⁵ can be obtained for an acceptor concentration of 6 molecules per sphere and an L:W ratio of 10. These values have to be compared to the experimental ones: if all of the pores between the spheres in Vycor are interconnected, the L:W ratio should be $200:40 = 5$. The concentration used by Even et al¹⁵ was 2-to-3 molecules/sphere, if one assumes a random distribution of donors and acceptors within the Vycor glass.

Our model oversimplifies the Vycor structure. The silicate spheres probably are randomly packed, and the microstructures of the pores are not known. Thus, one should not take our comparison with experiments too seriously. It is not the purpose of this study, however, to attempt to describe the Vycor structure, nor to compare our results with experimental observation. The main purpose of this work is to show that, if one studies one-step trapping process on a non-fractal (e.g., cubic) lattice with excluded volumes of length scales equal or greater than the characteristic energy transfer length, an apparent fractal behavior can be obtained over limited range of time (or acceptor concentrations). Of course, one can try to distinguish between a true fractal and an apparent fractal behavior if the experimental study is carried out over a long time scale. Most unfortunately, this is not possible due to the limitation imposed on the experimentalist by the finite lifetime of the excited state of the donor.

Extensions of this work to simulations of other interesting structures are now in progress, and the details of these simulations will be published later.

ACKNOWLEDGMENT

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References:

- (1) Klafter J., Blumen A., J. Chem. Phys. (1984), 80, 875
- (2) Mandelbrot B., "Les Objets Fractals" (Flammarion, Paris, 1975);
English versions: "Fractals: Form, Chance and Dimension", (W. H. Freeman, San Francisco, 1977); "The Fractal Geometry of Nature", (W. H. Freeman, San Francisco, 1982)
- (3) De Gennes P.-G., J. Chem. Phys. (1982), 76, 3316
- (4) Allen J. P., Colvin J. J., Stimson D. G., Flynn C. P., and Stapleton H. J., Biophys. J. (1982), 38, 299
- (5) Stapleton H. J., Allen J. P., Flynn C. P., Stimson D. G., Kurz S. R., Phys. Rev. Lett. (1980), 45, 1456
- (6) Avnir D., Farin D., J. Chem. Phys. (1983), 79, 3536
- (7) Witten T. A., and Sander L. M., Phys. Rev. Lett. (1981), 47, 1400, and Phys. Rev. (1983), B27, 5686
- (8) (a) Pietronero L., Wiesmann H. J., J. Stat. Phys. (1984), 36, 909
(b) Niemeyer L., Pietronero L., Wiesmann H. J., Phys. Rev. Lett. (1984), 52, 1033
- (9) (a) Ott E., Withers W. D., and Yorke J. A., J. Stat. Phys. (1984), 36, 687
(b) Procaccia I., J. Stat. Phys. (1984), 36, 649
- (10) (a) Wilkinson D., Willemsen J. F., J. Phys. (1983) A16, 3365
(b) Lenormand R., Cherbulin C., Zeccone C., C. R. Acad. Sc. Paris, Ser II, (1983), 297, 637
- (11) Alexander S. and Orbach R., J. Physique Lett. (1982), 43, L-625
- (12) Rammal R., and Toulouse G., J. Physique Lett. (1983), 44, L-13
- (13) (a) Klymko F. W. and Kopelman R., J. Phys. Chem. (1983), 87, 4565

- (b) Argyrakis P. and Kopelman R., Phys. Rev. (1984), B29, 511
- (c) Argyrakis P. and Kopelman R., J. Phys. Chem. (1984), 81, 1015
- (14) (a) Evesque P., J. Physique (1983), 44, 1217
- (b) Evesque P. and Duran J., J. Chem. Phys. (1984), 80, 3016
- (15) Even U., Rademann K., Jornter J., Manor N., Reisfeld R., Phys. Rev. Lett. (1984), 52, 2164
- (16) Kadokura K., "Phase Transformation of Submicron Particles in Porous Glass", Ph.D. Diss, (University of California, Los Angeles, 1983)
- (17) Inokuti M., Hirayama F., J. Chem. Phys. (1965), 43, 1978
- (18) Blumen A., Manz J., J. Chem. Phys. (1979), 71, 4694

Figure caption:

Fig. 1:

Plot of the $\ln(-\ln(\text{Intensity}))$ versus $\ln(\text{time})$ for different acceptor concentration P_A on a simple cubic lattice of rods of length:width ratio of 5 for top and 10 for the bottom figure. Dipolar Interaction ($s=6$) is assumed. I_D denotes the donor luminescence intensity; the slope of the curves defines an exponent d'/s which varies with time, and concentration as expected for non-fractal structure. $P_A = 20, P_A = 6, P_A = 2$. t is in arbitrary unit.

Fig. 2:

Plots of the calculated \ln of the donor intensity versus $t^{\langle d' \rangle/6}$ in a semi-log scale, where $\langle d' \rangle$ is the average fractional dimension value obtained from the averaging slope of Fig. 1. These results show that "fractal-like" behaviors can be observed over the range of time and concentration used experimentally if a structure similar to the one with which we approximated the Vycor structure is used. $P_A = 20, P_A = 6, P_A = 2$. t is in arbitrary unit.

Table 1: The dependence of $\langle d' \rangle$ (the average pseudo dimensionality) and the transfer time τ_0 on the acceptor concentration P_A and length:width ratio L/W . τ_0 is the time for which the donor intensity has decayed to $1/e$ of its initial value in unit of τ_1 , the characteristic time for a transfer between a donor and an acceptor separated by R_0 , the radius of the sphere.

L / W	5			10		
P_A	2	6	20	2	6	20
$\langle d' \rangle$	2.2	2.1	2	2.15	1.7	1.6
τ_0 / τ_1	$4.7 \cdot 10^{-3}$	$7.4 \cdot 10^{-3}$	$2.6 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$	$5.6 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$

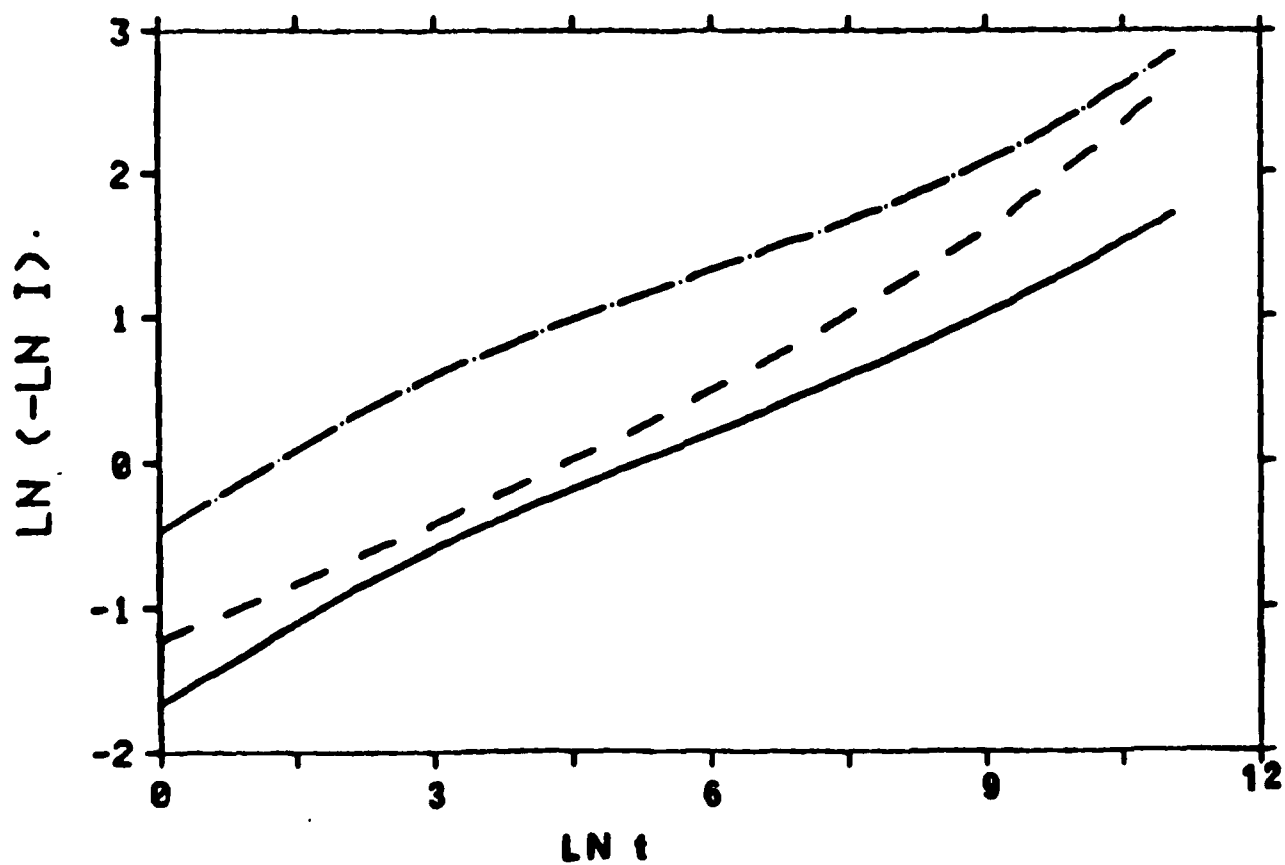
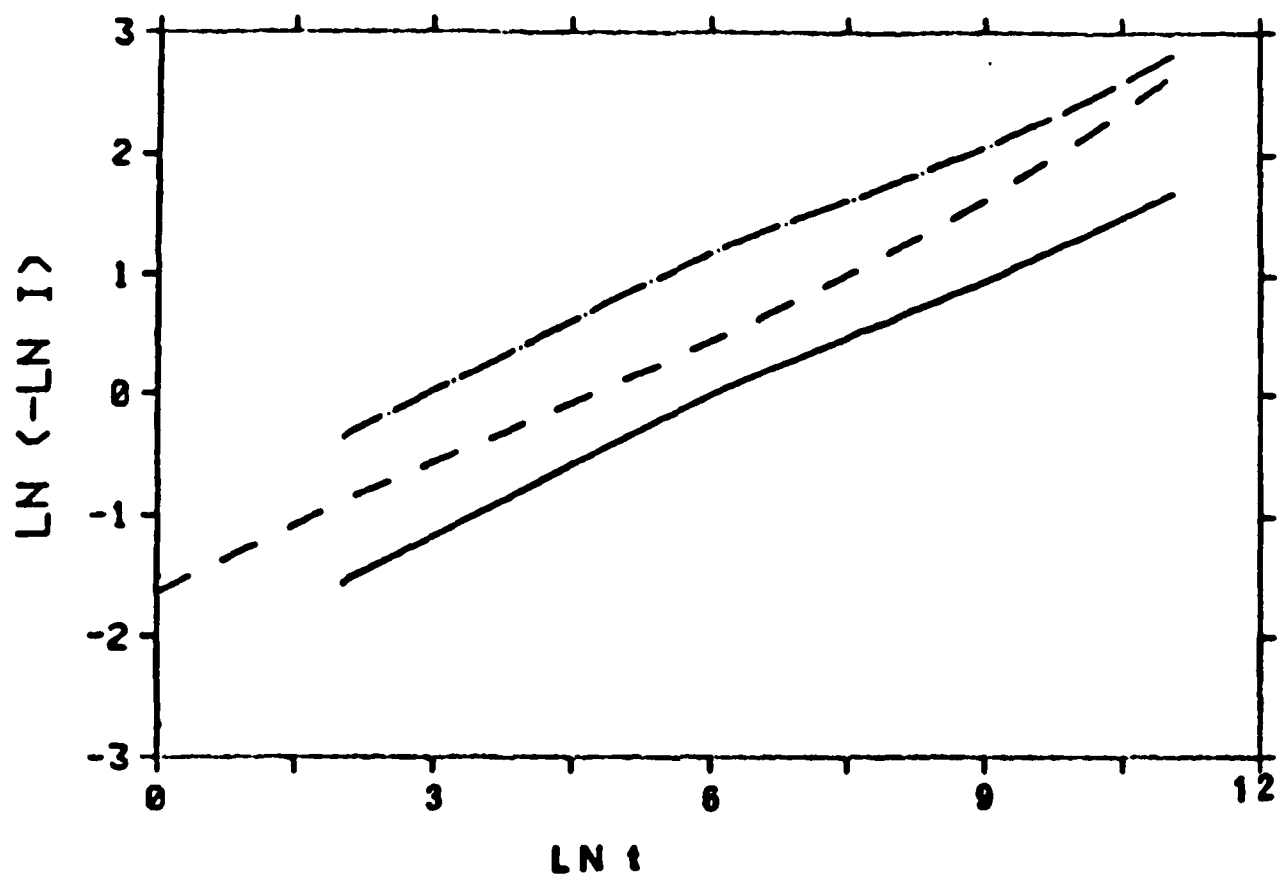


Fig 1

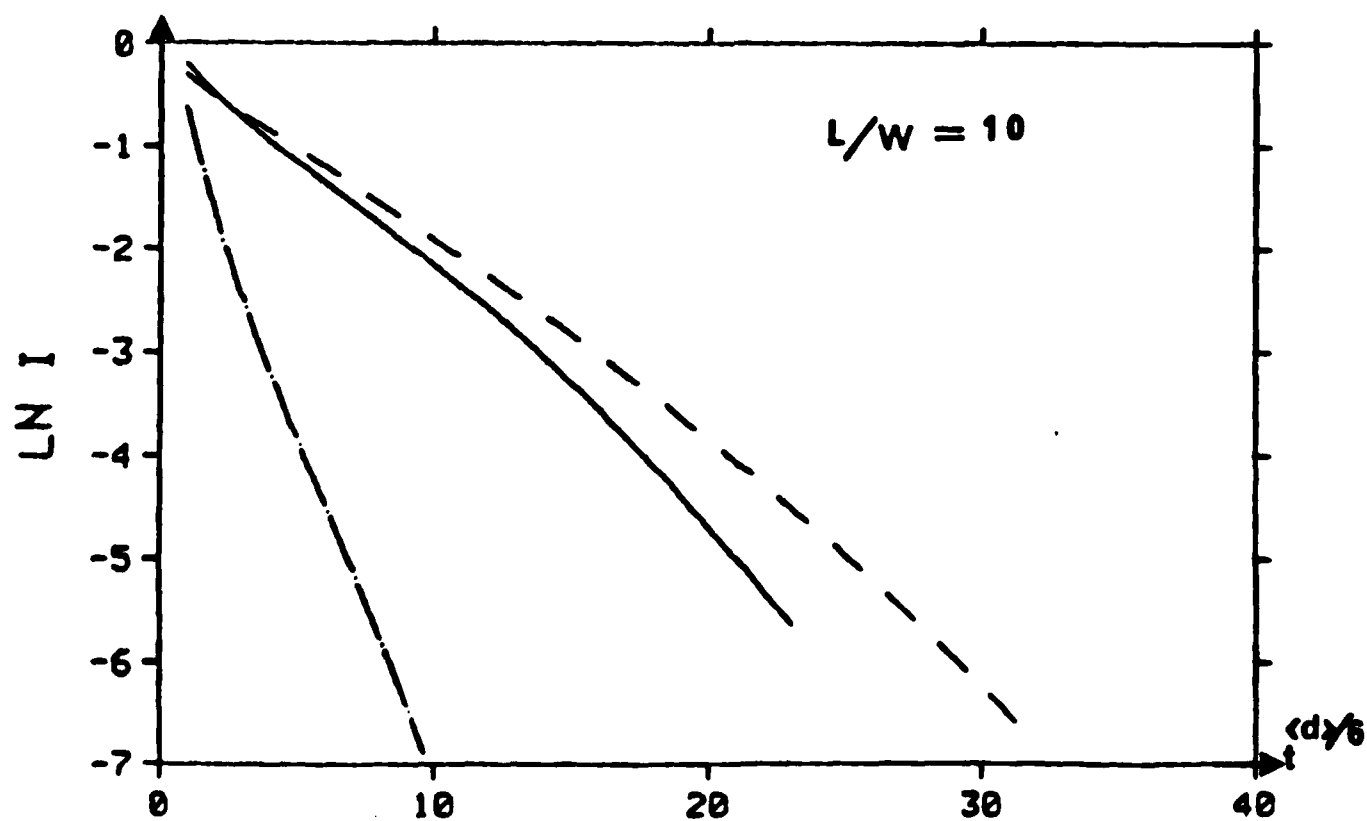
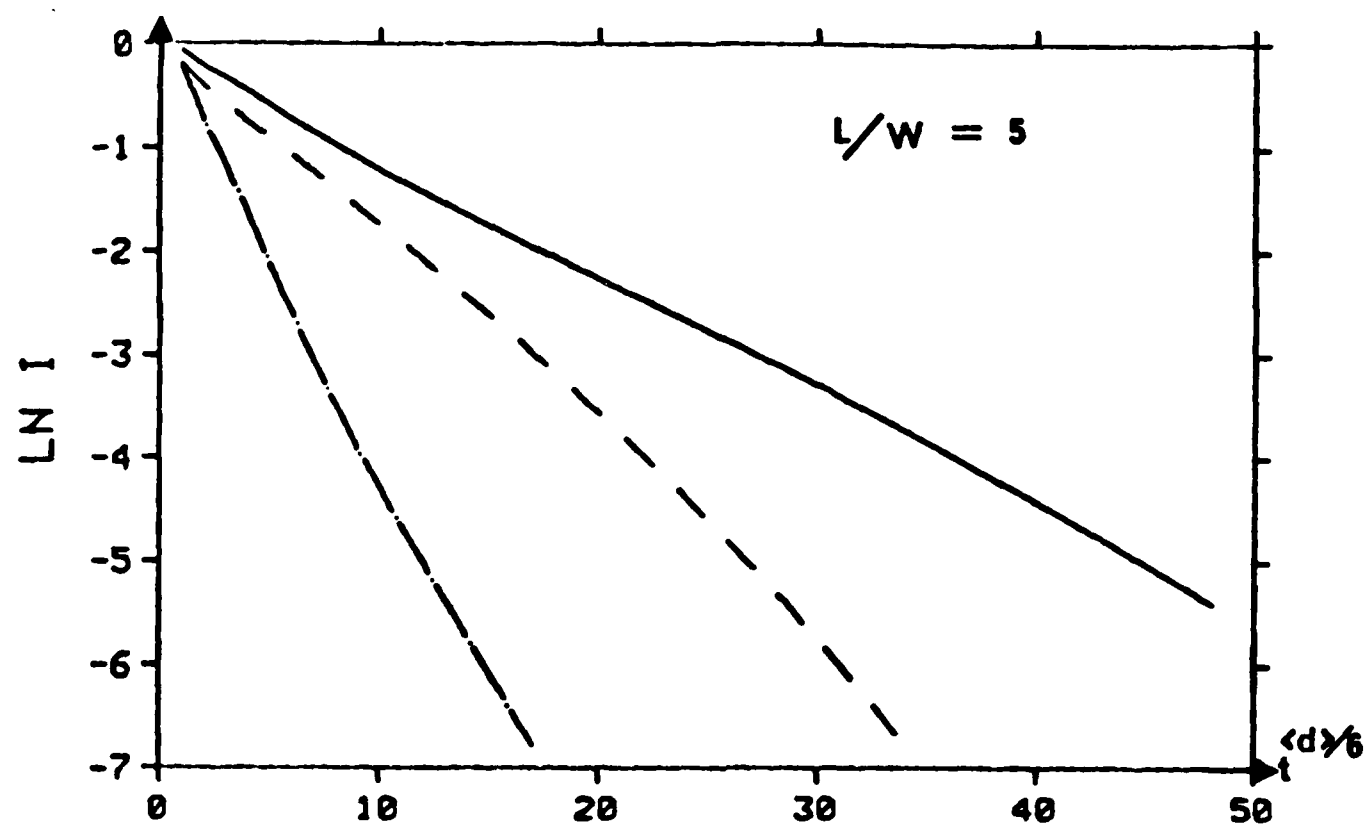


Fig.2

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